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A Research Note

A CONTAMINANT IN N-NITROSODIMETHYLAMINE CONFIRMATION BY HIGH RESOLUTION MASS SPECTROMETRY

INTRODUCTION

THE CARCINOGENICITY of N-nitrosamines poses a potential health hazard to humans. Reports of the presence of these compounds in foods, therefore, should be carefully validated, and evaluated, in order to reduce the possibility of spreading misleading information. Current indications are that N-nitrosamines, when found in foods, are present only in the μg/kg range. Analysis of such low concentrations requires precise methods for the recovery of the nitrosamines from the food product and specific, sensitive quantitative procedures. Although sensitive procedures, such as thin-layer and gas chromatography are available, contaminants from the solvents or from the food product may lead to erroneous identification of nitrosamines based on retention values or response to indicator sprays. Confirmation by other methods is desirable. Mass spectrometry, which gives a unique fragmentation pattern for a particular compound, appeared to be, at this time at least, the ultimate, specific procedure for the identification of trace amounts of nitrosamines. We are now reporting the possibility of confusing the identification of N-nitrosodimethylamine with the ^{13}C and ^{29}Si isotopes of trimethylsilyl ion when using high resolution mass spectrometry.

EXPERIMENTAL

IN A STUDY of the microbial formation of nitrosamines, the bacterial culture medium was shaken with methylene chloride to extract N-nitrosodimethylamine (DMNA) which had been produced. Severe foaming and emulsion formation interfered with the separation. A drop of Dow-Corning Anti-foam B was added. The final methylene chloride extracts, after washing with 0.1N HCl to remove basic interfering substances, were concentrated to 0.1–0.5 ml in a Kuderna-Danish concentrator and submitted for analysis by gas chromatography using a Carbowax 20M column and an alkali flame ionization detector as described previously (Wasserman et al., 1972).

RESULTS

WHEN A POSITIVE response for apparent DMNA was obtained the sample was examined by gas chromatography-mass spectrometry in order to confirm the presence of the nitrosamine. The DuPont MS 21-492, adjusted to a resolution of 1:12000, was used in the peak matching mode in which the mass of an unknown ion is compared to that of a standard and the mass of the unknown is measured very accurately. Two mass spectral peaks were obtained from the extracts of the culture medium; the first, a small peak, reached a maximum and diminished slightly, then was followed immediately by a very large peak. Initially, it was not known which response could be attributed to DMNA, since only one peak was discernible by either the alkali flame ionization or the flame ionization detectors of the gas chromatograph, apparently indicating the presence of a single compound. Upon resorting to peak matching with the mass spectrometer we determined that the first peak had an m/e = 74.048 and the large, second peak an m/e = 74.046. When the material was re-run in the mass spectrometer at low resolution the readily recognizable isotopic pattern of a silicon-containing compound was evident at m/e 73, 74 and 75. DMNA has an m/e = 74.0480; the ^{13}C isotope of the trimethylsilyl ion has an m/e = 74.0502, and the ^{29}Si isotope has an m/e = 74.0469. The range among them is three parts in 74000.

The Dow-Corning Anti-foam B used in the extraction procedure contains a silicone compound; however, the identity of the silicon-containing compound that has essentially the same GLC retention time as DMNA was not established.

The presence of an ion with a mass: charge ratio so similar to that of DMNA may be misleading in high resolution confirmation studies for trace quantities of DMNA particularly when it is realized that trimethyl silyl derivatives are used to silanize GC columns or the GC-MS interfacing lines to prevent adsorbtion. Silicone compounds are also used in food packaging materials and may become contaminants of the packaged product. Fragmentation of these compounds in the mass spectrometer then can result in the formation of trimethylsilyl ions, as detailed by Biemann (1962).

False positive identification of DMNA could possibly be avoided by resorting to one or more of the following: (1) Utilizing gas chromatographic column coatings other than Carbowax 20M to achieve separation of DMNA from the silicon-containing compound; (2) Use the alkali flame ionization detector to differentiate N-containing compounds; (3) Low resolution mass spectral analysis of fairly pure preparations to obtain the entire fragmentation pattern, and (4) Monitor two specific ion peaks for DMNA, i.e., m/e = 74.048 and 42.034, in the high resolution mode.

During the preparation of this paper Gough and Webb (1973) also reported observing fragment ions corresponding to the trimethylsilyl group in some food extracts. Under their conditions, however, this material was not eluted from the GC at the same time as N-nitrosodimethylamine, and would not be mistaken for the nitrosamine if a nitrogen-specific detector was used.

REFERENCES

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Ms received 6/15/73; revised 7/14/73; accepted 7/16/73.